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The $^2\Sigma^+ - ^2\Pi$ separation in KO

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Abstract

The $^2\Sigma^+ - ^2\Pi$ separation in KO is investigated using large basis sets and high levels of correlation treatment. Relativistic effects are included at the Dirac-Fock level and reduce the separation only slightly. The basis set superposition error is considered in detail. On the basis of these calculations, our best estimate places the $^2\Pi_{3/2}$ state about 200 cm^{-1} above the ground $^2\Sigma^+$ state in agreement with our previous estimate.

I. Introduction

In 1986 we computed the $^2\Sigma^+ - ^2\Pi$ separation in KO to be 238 cm^{-1} with the $^2\Sigma^+$ state being the lower of the two [1]. This separation was computed at the singles and doubles configuration interaction (SDCI) level using a large Slater basis set. While not definitive, the separation was thought to be accurate because of the small difference between the SDCI and self-consistent-field (SCF) values. However, when 15 electrons are correlated, an SDCI treatment can underestimate the differential correlation effects. Approaches such as the modified coupled-pair functional (MCPF) method [2], or the coupled cluster singles and doubles method with a perturbational estimate of the triple excitations [3] [CCSD(T)], account for the effect of higher than double excitations and can therefore yield superior results to the SDCI approach.

Experimentally, the ground state has not been determined and there is conflicting evidence. The failure to observe an electron spin resonance (ESR) spectrum [4] is consistent with a $^2\Pi$ ground state, while the magnetic deflection experiments [5] suggest a $^2\Sigma^+$ ground state. Photoelectron detachment experiments [6] on KO^-

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might offer a mechanism to directly observe both states, and hence determine the ground state and the separation; such experiments [6] have recently been performed for NaO^- and preliminary results suggest that they are possible for all of the alkali oxides systems. In addition, microwave experiments [7] have recently been performed on NaO and, with a pure-precession hypothesis, an estimate of the $^2\Sigma^+ - ^2\Pi$ separation was obtained. An analogous experiment should be possible for KO .

Given the recent experimental activity on the alkali oxides, it seems timely to reinvestigate the $^2\Sigma^+ - ^2\Pi$ separation in KO at higher levels of theory. We consider the effect of one-particle basis set and basis set superposition error (BSSE) in more detail than in our previous work. In addition, the separation between the $^2\Sigma^+$ and $^2\Pi$ states is small enough that relativistic effects could affect the ordering of the states. These were not included in the previous work and are addressed here.

II. Methods

Two basis sets are used in this work. The small oxygen basis set is the $(13s\ 9p\ 6d\ 4f)/[5s\ 5p\ (2+1)d\ 1f]$ atomic natural orbital [8] (ANO) set [9] determined from the average natural orbitals of O and O^- . (The notation $n+m$ indicates n ANO orbitals are employed and m primitive functions are uncontracted). In the large oxygen basis set only two s and one p ANOs are used. The outer five s and five p primitives and the d and f polarization functions are uncontracted. This is augmented with two uncontracted g functions and a diffuse s function with an orbital exponent of 0.076666. Thus the final basis set is of the form $(14s\ 9p\ 6d\ 4f\ 2g)/[(2+6)s\ (1+5)p\ 6d\ 4f\ 2g]$.

The small K basis is derived from the $(24s\ 15p)$ basis [10] augmented with an s function optimized for K^- and three p functions optimized for the 2P state of K . The s and p basis sets are contracted to $(3+6)$ and $(2+7)$, respectively, where the three s and two p contraction coefficients are taken from the SCF wave function. The basis is further augmented with six even-tempered ($\alpha_n = 2.5^n \alpha_0$ for $n=0,k$) d functions with $\alpha_0 = 0.0455$ and four even-tempered f functions with $\alpha_0 = 0.12949$. The small K basis set is of the form $(25s\ 18p\ 6d\ 4f)/[(3+6)s\ (2+7)p\ 6d\ 4f]$. In the large K basis set, the s and p functions are contracted $(2+12)$ and $(2+9)$ and two g functions ($\alpha = 0.768$ and 0.307) are added, thus yielding a basis set of the form $(25s\ 18p\ 6d\ 4f\ 2g)/[(2+12)s\ (2+9)p\ 6d\ 4f\ 2g]$. Only the pure spherical harmonic components of the basis functions are used.

The orbitals are optimized using the SCF approach. We have treated the $^2\Pi$ state using symmetry and equivalence restrictions (i.e., a $\pi_x^{1.5}\pi_y^{1.5}$ occupation) or by using a symmetry broken solution (i.e., a $\pi_x^2\pi_y^1$ occupation). Electron correlation is added using the MCPF or CCSD(T) approaches. Fifteen electrons are correlated, corresponding to the O $2s$ and $2p$ and the K $3s$, $3p$, and $4s$ electrons.

Relativistic effects are estimated as the difference between the SCF and Dirac-Fock (DF) results. Because correlation was not included, it was possible to reduce the basis set size without affecting the accuracy of the results. The full s and p primitive basis sets for K and O were contracted to $[(3+6)s(2+7)p]$ and $[(2+3)s(1+4)p]$ using the orbitals from the SCF wave functions for K^+ and O^- . For polarization the $6d$ set and the outer three of the $4f$ functions on K were used, and on O the outer 3 primitive d functions and the f function with the largest coefficient from the ANO polarization set were used. The SCF $^2\Sigma^+ - ^2\Pi$ separation in this basis set was identical to that found using the small ANO set.

The SCF/MCPF calculations were performed using the SEWARD [11]-SWEDEN [12] program system. The CCSD(T) calculations were performed using the program developed by Scuseria [13]. The atomic DF calculations were performed using GRASP [14] while the molecular calculations were performed using the code developed by Dylla [15]. All calculation were performed on the NASA Ames Central Computer Facility CRAY Y-MP or Computational Chemistry Branch IBM RISC System/6000 computers.

III. Results and Discussion

The separation at the SCF level is only slightly larger than in our previous work [1], with the big basis set result essentially reaching our previous estimate of 250 cm^{-1} for the numerical Hartree-Fock separation. The SDCI separation in the small basis set is only 6 cm^{-1} smaller than that reported in our previous study. With a symmetry broken SCF solution, the $^2\Pi$ state is predicted to be below the $^2\Sigma^+$ state. When correlation is added at the SDCI level, the $^2\Sigma^+$ state is predicted to be lower. However, the SDCI based on the symmetry broken SCF orbitals yields a significantly smaller separation. This suggests that the SDCI approach is unable to overcome the bias in the SCF wave function. At the MCPF level, the effect of symmetry breaking is smaller, as expected, since the MCPF approach includes the effect of higher excitations. At this level, the symmetry broken solution actually

leads to a larger separation than using the SCF with symmetry and equivalence restrictions. Both MCPF separations are about 100 cm^{-1} smaller than the SDCl result with symmetry and equivalence restrictions. The CCSD separation is the same as the MCPF. The effect of triples is to further increase the separation by 47 cm^{-1} , which is almost an order of magnitude smaller than the difference between the SCF and CCSD (368 cm^{-1}). This strongly suggests that even higher levels of theory will not significantly increase the correlation contribution to the separation. Expanding the basis set results in a small increase in both SCF and MCPF separations.

In Table II we report the BSSE at the MCPF level. We compute the BSSE for K^+ with the O basis set, $\text{K}^+(\text{O})$, and O^- with the K basis set, because both states of the molecule at r_e are best described as K^+O^- . K^+ is a closed shell; therefore the calculation of the BSSE is straightforward, and we consider $\text{K}^+(\text{O})$ at the two relevant internuclear separations. The $2p^5$ occupation of O^- is oriented $2p\sigma^2 2p\pi^3$ and $2p\sigma^1 2p\pi^4$ for the $^2\Pi$ and $^2\Sigma^+$ states, respectively. As shown in previous work [16], the BSSE can differ significantly for the two occupations. Therefore we use the BSSE for the $2p\sigma^2 2p\pi^3$ occupation to correct the $^2\Pi$ state and the BSSE for the $2p\sigma^1 2p\pi^4$ occupation to correct the $^2\Sigma^+$ state.

For K^+ the BSSE is small for both basis sets. It is slightly larger for the $^2\Sigma^+$ state than the $^2\Pi$ state because of the shorter bond length. In contrast, the O^- BSSE is much larger for the smaller basis set. In spite of the longer bond length, the $\text{O}^-(\text{K})$ BSSE is larger for the $^2\Pi$ state, because a pair of oxygen $2p\sigma$ electrons points at the ghost basis set compared with only one electron in the $^2\Sigma^+$ state. For both basis sets the total BSSE is very similar for the $^2\Sigma^+$ and $^2\Pi$ states and therefore does not have an important differential effect on the separation. Given the small total BSSE for the big basis set, this conclusion seems definitive in spite of any uncertainties in how to best compute the BSSE.

One effect not considered to this point is relativity. The spin-orbit splitting in the O^- ion was calculated to be 193 cm^{-1} at the Dirac-Coulomb level. Inclusion of the Breit interaction decreased the splitting to 170 cm^{-1} . This value is expected to be accurate as an analogous treatment of O agrees with experiment to within 2 cm^{-1} . Because the bonding in KO is best described as K^+O^- , this splitting in O^- can be used in a simple first-order model [17] to estimate the splitting in KO. On this basis, the $^2\Sigma_{1/2}^+$ state is unshifted from its nonrelativistic position, the $^2\Pi_{1/2}$

state is shifted up by 57 cm^{-1} and the $^2\Pi_{3/2}$ state is shifted down by 57 cm^{-1} .

Mixing of K $4s$ character from covalent contributions to the wave functions and spin-orbit mixing of the $^2\Pi_{1/2}$ and $^2\Sigma_{1/2}^+$ states could invalidate the first-order model. Therefore we study the $^2\Pi_{3/2}$ and $^2\Sigma_{1/2}^+$ states at the Dirac-Fock level. On the basis of the nonrelativistic calculations we use a bond length of $4.4 a_0$ for the $^2\Pi_{3/2}$ state and $4.13 a_0$ for the $^2\Sigma_{1/2}^+$ state. At this level, the $^2\Pi_{3/2}$ state is lowered by 36 cm^{-1} and the $^2\Sigma_{1/2}^+$ state is lowered by 24 cm^{-1} , relative to the nonrelativistic states. Thus the differential effect of relativity on the state separation is only 12 cm^{-1} , or about $1/5$ of the estimate derived from O^- . Clearly, however, the differential effect of relativity is sufficiently small that it will not reverse the order of the states computed at the nonrelativistic level.

Our best separation is obtained by correcting the CCSD(T) separation for: 1) MCPF basis set improvement ($+36 \text{ cm}^{-1}$), 2) BSSE ($+8 \text{ cm}^{-1}$) and 3) relativistic effects (-12 cm^{-1}). This yields a separation of 214 cm^{-1} , with the $^2\Sigma^+$ state being lower. This is very similar to our previous result [1]. While it is difficult to be definitive for a separation this small, the calculations strongly suggest that the ground state is $^2\Sigma^+$. Because improving the basis set increases the separation, as does including higher levels of correlation treatment, and relativistic effects are very small, it is difficult to imagine what effect would reverse the order of these two states.

IV. Conclusions

The separation at our highest level of theory, the CCSD(T) approach, is 182 cm^{-1} . Including the correction for basis set incompleteness from the MCPF level increases the separation to 218 cm^{-1} , which is very similar to our previous result [1]. The differential effect of BSSE is 8 cm^{-1} , increasing the separation. Relativistic effects reduce the separation by only 12 cm^{-1} . Thus we conclude that the ground state is $^2\Sigma^+$.

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Table I. Spectroscopic constants for the $^2\Sigma^+$ and $^2\Pi$ states of KO.

	$^2\Sigma^+$		$^2\Pi$		$^2\Pi$ sym broken			
	$r_e(a_0)^a$	$\omega_e(\text{cm}^{-1})$	$r_e(a_0)$	$\omega_e(\text{cm}^{-1})$	$T_e(\text{cm}^{-1})$	$r_e(a_0)^a$	$\omega_e(\text{cm}^{-1})$	$T_e(\text{cm}^{-1})$
Small basis								
SCF	4.202	412	4.441	399	222	4.442	399	-236
SDCI	4.133	426	4.400	397	232	4.401	397	43
MCPF	4.132	422	4.419	390	92	4.418	391	135
CCSD	(4.130)					(4.400)		135
CCSD(T)	(4.130)					(4.400)		182
Large basis								
SCF	4.202	412	4.440	399	248			
MCPF	4.117	422	4.404	391	128			

^aValues in parenthesis indicate that the geometry is not optimized.

Table II. Summary of the BSSE at the MCPF level.

	BSSE(cm^{-1})
Small basis set	
$^2\Sigma^+$	
$\text{K}^+(\text{O})$ at $r=4.13$	32.1
$\text{O}^-(\text{K})$ at $r=4.13$	348.4
Total	380.5
$^2\Pi$	
$\text{K}^+(\text{O})$ at $r=4.40$	20.9
$\text{O}^-(\text{K})$ at $r=4.40$	364.5
Total	385.4
Big basis set	
$^2\Sigma^+$	
$\text{K}^+(\text{O})$ at $r=4.13$	32.5
$\text{O}^-(\text{K})$ at $r=4.13$	88.5
Total	121.0
$^2\Pi$	
$\text{K}^+(\text{O})$ at $r=4.40$	25.8
$\text{O}^-(\text{K})$ at $r=4.40$	103.4
Total	129.2